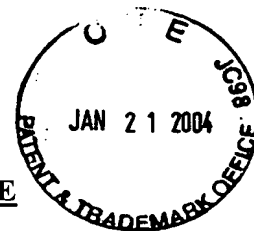


Docket No: 230112US26



**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

IN RE APPLICATION OF: Tomoyo YAMAGUCHI, et al.

SERIAL NO: 10/607,537

ATTN: BOX MISSING PART

FILED: June 27, 2003

FOR: PLASMA PROCESSING METHOD

**FILING OF CERTIFIED ENGLISH TRANSLATION UNDER 37 CFR 1.52(d)**

COMMISSIONER FOR PATENTS  
ALEXANDRIA, VIRGINIA 22313

SIR:

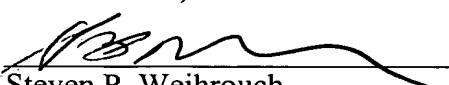
Responsive to the Notice to File Missing Parts of Application (Form PTO-1533) dated November 26, 2003, Applicants submit herewith a certified English translation of the application, as filed, in accordance with the provisions of 37 C.F.R. §1.52(d).

Also submitted herewith are verified English translations of the two prior Provisional Application No. 60/420,788 filed October 24, 2002 and 60/423,566 filed November 5, 2002.

In light of the foregoing, this application is deemed to be in proper condition for examination and such favorable action is earnestly solicited.

Respectfully submitted,

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**The PTO did not receive the following  
listed item(s) PAGE 1 - 74 OF SPECIFICATION**

applied to the upper electrode 21 and the lower electrode or susceptor 5 to turn the etching gas into plasma, thereby etching the antireflective layer 182 on the process subject W (FIG. 13A). As a consequence, the remaining film quantity of the photoresist layer 183 becomes large after the etching of the antireflective layer 182, thereby allowing a hole or groove formed in the following etching step of the etching objective portion to have a desired opening shape.

An example of a substance having C and F used in this etching is  $\text{CF}_4$ , with which the ArF photoresist layer is less damaged. As a substance having H, a hydrocarbon,  $\text{H}_2$ , or hydrofluorocarbon may be used. An example of a hydrocarbon is  $\text{CF}_4$ . A preferable hydrofluorocarbon is a substance, in which the ratio of the number of H atoms relative to the number of F atoms is three or more, and an example of such a substance is  $\text{CH}_3\text{F}$ . Where  $\text{CH}_3\text{F}$  is used, the ratio of the flow rate of  $\text{CH}_3\text{F}$  relative to the flow rate of a substance having C and F is set at 0.04 to 0.07 in the etching gas. With this arrangement, the remaining film quantity of the ArF photoresist layer is considerably increased after the etching of the antireflective layer, as compared to the case of using no  $\text{CH}_3\text{F}$ .

Before or after the timing when the high-frequency powers are applied to the upper and lower electrodes, a

DC voltage is applied from the DC power supply 13 to the electrode 12 in the electrostatic chuck 11 to electrostatically attract and hold the process subject W on the electrostatic chuck 11. After the etching of the antireflective layer 182 described above is finished, the etching gas and high-frequency powers stop being supplied.

Then, another etching gas, such as a mixture gas of  $C_5F_8$ ,  $O_2$ , and Ar, is supplied into the process container 2, thereby setting the pressure in the process container 2 at a predetermined value, such as 2.00 Pa (15 mTorr). Also, high-frequency powers are applied to the upper electrode 21 and the lower electrode or susceptor 5 to turn the etching gas into plasma, thereby etching the  $SiO_2$  layer 181 on the process subject W (FIG. 13B). During the etching, an end-point detector (not shown) is used to detect a predetermined light intensity, so that the etching is finished based thereon.

The etching objective portion is not limited to the  $SiO_2$  layer described above. This may be applied to etching of oxide film (oxygen compound) such as TEOS, BPSG, PSG, SOG, thermal oxidation film, HTO, FSG, organic Si oxide film, CORAL (Novellus Systems), low dielectric constant organic insulating film, or the like. Also, the structure of the plasma processing apparatus used is not limited to that shown in FIG. 1.

Next, an explanation will be given of present examples according to this embodiment.

The process subject W used had an  $\text{SiO}_2$  layer (with a film thickness of 2  $\mu\text{m}$ ), an antireflective layer (with a film thickness of 60 nm) covering the  $\text{SiO}_2$  layer, and an ArF photoresist layer (with a film thickness of 360 nm) covering the antireflective layer, as shown in FIG. 13A.

In the present examples, the etching of the antireflective layer was performed under the following conditions. Specifically, the pressure in the process container 2 was set at 6.66 Pa (50 mTorr); the etching gas was a mixture gas of  $\text{CF}_4$  (at a flow rate of 100 mL/min (sccm)) and  $\text{CH}_3\text{F}$  (at a flow rate of 4 or 7 mL/min (sccm)); a high-frequency power applied to the upper electrode from a high-frequency power supply having a frequency of 60 MHz at 1,000 W; and a high-frequency power applied to the lower electrode from a high-frequency power supply having a frequency of 2 MHz at 100W. Furthermore,  $\text{CH}_3\text{F}$  was replaced with  $\text{H}_2$  (at a flow rate of 5, 10, or 15 mL/min (sccm)),  $\text{CH}_2\text{F}_2$  (at a flow rate of 5 or 10 mL/min (sccm)), or  $\text{CHF}_3$  (at a flow rate of 10, 30, 50, or 70 mL/min (sccm)) in the etching gas to perform the same etching.

On the other hand, a comparative example was prepared to use an etching gas only of  $\text{CF}_4$  (at a flow rate of 100 mL/min (sccm)), while using the other

etching conditions the same as those of the present examples.

The etching of the antireflective film 182 was performed under the conditions described above  
5 according to the present examples and comparative example. After a lapse of a constant etching time, a remaining film thickness of the ArF photoresist layer was measured, which showed the following results.

In the present examples, where  $\text{CH}_3\text{F}$  was used, a  
10 flow rate of 4 mL/min resulted in 375 nm, and 7 mL/min resulted in 405 nm. Where  $\text{H}_2$  was used, a flow rate of 5 mL/min resulted in 345 nm, and 10 mL/min and 15 mL/min resulted in 360 nm. Where  $\text{CH}_2\text{F}_2$  was used, a flow rate  
15 of 5 mL/min resulted in 345 nm, and 10 mL/min resulted in 400 nm. Where  $\text{CHF}_3$  was used, a flow rate of 10 mL/min resulted in 350 nm, 30 mL/min resulted in 360 nm, 50 mL/min resulted in 360 nm, and 70 mL/min resulted in 390 nm. On the other hand, the comparative example resulted in 330 nm.

20 As described above, it was confirmed that any of the present examples showed a remaining film thickness larger than the comparative example. This reason seems that F active species for etching the ArF photoresist layer suitably reacted with H active species generated  
25 from a gas containing H, and formed gases, such as HF, which were then exhausted out of the process container.

Of the present examples,  $\text{CH}_3\text{F}$  was particularly

excellent. In this case, the reason of a large remaining film quantity in spite of a low flow rate of  $\text{CH}_3\text{F}$  seems to be attributed to the number of H atoms larger than the number of F atoms in molecules. In the case of  $\text{H}_2$ , the remaining film quantity was smaller than other substances. This is so, because  $\text{H}_2$  is a chemically stable substance, and H active species once generated seem to preferentially react and re-combine with other H active species, rather than reacting with F active species.

Accordingly, it was confirmed that the etching gas preferably contained a substance that was relatively unstable and had a lot of H atoms therein, such as a hydrocarbon ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , or the like) or hydrofluorocarbon (particularly a composition in which the ratio of the number of H atoms relative to the number of F atoms is three or more, such as  $\text{CH}_3\text{F}$ ). It was also confirmed that, where  $\text{CH}_3\text{F}$  was used, the remaining film quantity was increased, even if the ratio of the flow rate of  $\text{CH}_3\text{F}$  relative to the flow rate of  $\text{CF}_4$ , i.e., a substance having C and F, was set at a low value of 0.04 to 0.07.

(Eighth embodiment)

In this embodiment, the plasma processing apparatus 1 shown in FIG. 1 is used to process a process subject W shown in FIG. 14A. This process subject W has an  $\text{SiO}_2$  layer 191 disposed as an etching objective, an antireflective layer 192 covering the  $\text{SiO}_2$

layer 191, and a photoresist layer 193 of an ArF photoresist or F2 photoresist covering the antireflective layer 192. This process includes a step of etching the antireflective layer 192 through an opening pattern 193a of the photoresist layer 193, and a step performed thereafter of etching the SiO<sub>2</sub> layer 191. Also in this embodiment, the ArF photoresist or F2 photoresist may be made of an alicyclic group-containing acrylate resin, cycloolefin resin, or cycloolefin-maleic anhydride resin. As the antireflective layer, an organic polymeric material or amorphous carbon may be used.

The gate valve 32 is first opened, and the process subject W is transferred into the process container 2 and placed on the electrostatic chuck 11. Then, the gate valve 32 is closed, and the pressure in the process container 2 is reduced by the exhaust device 35. Then, the valve 28 is opened, and a first etching gas containing a substance having C and F, and CO, such as a mixture gas of CF<sub>4</sub> and CO, is supplied from the process gas supply source 30, thereby setting the pressure in the process container 2 at a predetermined value, such as 13.3 Pa (100 mTorr). In this state, high-frequency powers are applied to the upper electrode 21 and the lower electrode or susceptor 5 to turn the first etching gas into plasma, thereby etching the antireflective layer 192 on the process subject W

(FIG. 14A). Before or after the timing when the high-frequency powers are applied to the upper and lower electrodes, a DC voltage is applied from the DC power supply 13 to the electrode 12 in the electrostatic chuck 11 to electrostatically attract and hold the process subject W on the electrostatic chuck 11. After the etching of the antireflective layer 192 is finished, the etching gas and high-frequency powers stop being supplied.

Then, a second etching gas, such as a gas containing a fluorocarbon, e.g.,  $C_5F_8$  or  $C_4F_6$ , specifically a mixture gas of  $C_5F_8$  or  $C_4F_6$ ,  $O_2$ , and Ar, is supplied into the process container 2, thereby setting the pressure in the process container 2 at a predetermined value of the second etching, such as 2.00 Pa (15 mTorr). Also, high-frequency powers are applied to the upper electrode 21 and the lower electrode or susceptor 5 to turn the second etching gas into plasma, thereby etching the  $SiO_2$  layer 191 on the process subject W (FIG. 14B). During the etching, an end-point detector (not shown) is used to detect a predetermined light intensity, so that the etching is finished based thereon.

The etching objective portion is not limited to the  $SiO_2$  layer described above. This may be applied to etching of oxide film (oxygen compound) such as TEOS, BPSG, PSG, SOG, thermal oxidation film, HTO, FSG,



organic Si oxide film, CORAL (Novellus Systems), low dielectric constant organic insulating film, or the like. Also, the structure of the plasma processing apparatus used is not limited to that shown in FIG. 1.

5           Next, an explanation will be given of present examples according to this embodiment.

A process subject used was prepared as shown in FIG. 14A. In the present examples, the first etching was performed under the following conditions.

10           Specifically, the pressure in the process container was set at 6.66 Pa (50 mTorr) or 13.3 Pa (100 mTorr); the flow rate of the first etching gas  $\text{CF}_4$  at 75, 100, or 200 mL/min (sccm) and CO at 25, 100, or 200 mL/min (sccm); a high-frequency power applied to the upper  
15           electrode from a high-frequency power supply having a frequency of 60 MHz at 1,000, 1,500, or 2,000W; and a high-frequency power applied to the lower electrode from a high-frequency power supply having a frequency of 2 MHz at 100W.

20           In a comparative example, the first etching was performed under the following conditions. Specifically, the pressure in the process container was set at 6.66 Pa (50 mTorr), the first etching gas was only of  $\text{CF}_4$  (no CO contained) at a flow rate of 100 mL/min (sccm), and  
25           high-frequency power supplies were used with the same frequencies and at the same powers as those of the present examples.

In the present examples and comparative example, the second etching was performed under the following conditions. Specifically, the pressure in the process container was set at 2.00 Pa (15 mTorr); the flow rate of the second etching gas  $C_5F_8$ ,  $O_2$ , and Ar respectively at 15, 19, and 380 mL/min (sccm); a high-frequency power applied to the upper electrode from a high-frequency power supply having a frequency of 60 MHz at 2,170W; and a high-frequency power applied to the lower electrode from a high-frequency power supply having a frequency of 2 MHz at 1,550W.

The first etching and second etching were performed under the conditions described above, which gave the following results. Specifically, the present examples were far better than the comparative example in the selectivity of the  $SiO_2$  layer relative to the ArF photoresist layer (the etching rate of the  $SiO_2$  layer / the etching rate of the ArF photoresist layer). For example, in the present examples, where the first etching was performed under conditions with the pressure set at 13.3 Pa (100 mTorr), the  $CF_4$  flow rate at 75 mL/min (sccm), the CO flow rate at 25 mL/min (sccm), and the applied power to the upper electrode at 1,000W, the selectivity was 9.7. On the other hand, in the comparative example, the selectivity was 6.3.

Where  $C_5F_8$  was replaced with  $C_4F_6$  in the second etching step, the present examples (the first etching

gas was  $\text{CF}_4$  and  $\text{CO}$ ) were better than the comparative example (the first etching gas was only  $\text{CF}_4$ ) in the selectivity.

5 It seems that a protection film having inter-carbon bonds is formed on the surface of the ArF photoresist layer by plasma of a gas containing a substance having C and F, and  $\text{CO}$ . Accordingly, the plasma resistance of the ArF photoresist layer is improved only by irradiating the surface of the ArF  
10 photoresist layer with plasma of a gas containing a substance having C and F, and  $\text{CO}$ .

The present invention may be applied to a mask layer other than the ArF photoresist layer, although plasma resistance improvement effect cannot be expected  
15 so much, as compared to the ArF photoresist layer.

Furthermore, the second etching gas is not limited to a gas containing  $\text{C}_5\text{F}_8$  or  $\text{C}_4\text{F}_6$ , but may be formed of a gas containing another fluorine-containing compound, such as a fluorocarbon or hydrofluorocarbon.

20 (Ninth embodiment)

In this embodiment, the plasma processing apparatus 1 shown in FIG. 1 is used to process a process subject W shown in FIG. 15. This process subject W has an  $\text{SiO}_2$  layer 201 disposed as an etching  
25 objective, an organic antireflective layer 202 covering the  $\text{SiO}_2$  layer 201, and a photoresist layer 203 of an ArF photoresist or F2 photoresist covering the organic

antireflective layer 202 and having an opening pattern 203a formed therein. This process includes a step of plasma-etching the organic antireflective layer 202 through the opening pattern of the photoresist layer 203, and a step performed thereafter of plasma-etching the SiO<sub>2</sub> layer 201. Also in this embodiment, the ArF photoresist or F2 photoresist may be made of an alicyclic group-containing acrylate resin, cycloolefin resin, or cycloolefin-maleic anhydride resin. The organic antireflective layer 202 is made of, e.g., an organic polymeric material.

The gate valve 32 is first opened, and the process subject W is transferred into the process container 2 and placed on the electrostatic chuck 11. Then, the gate valve 32 is closed, and the pressure in the process container 2 is reduced by the exhaust device 35. Then, the valve 28 is opened, and an etching gas containing SiF<sub>4</sub> used as an Si-containing substance is supplied from the etching gas supply source 30, thereby setting the pressure in the process container 2 at a predetermined value. In place of SiF<sub>4</sub>, another substance having Si may be used, but SiF<sub>4</sub> is preferable to obtain a high etching rate of the organic antireflective layer 202. The etching gas may contain CHF<sub>3</sub>, HBr, He, or H<sub>2</sub> in addition to an Si-containing substance, and may consist of, e.g., SiF<sub>4</sub> and H<sub>2</sub>.

In this state, high-frequency powers are applied

from the first and second high-frequency power supplies 40 and 50 to turn the etching gas into plasma, thereby etching the organic antireflective layer 202 through the opening pattern 203a of the photoresist layer 203.

5 Before or after the timing when the high-frequency powers are applied from the first and second high-frequency power supplies 40 and 50, a DC voltage is applied to the electrode 12 in the electrostatic chuck 11 to electrostatically attract and hold the process  
10 subject W on the electrostatic chuck 11. After the etching is performed for a predetermined time, the high-frequency powers and etching gas stop being supplied, so that the etching of the organic antireflective layer 202 is finished. An end-point  
15 detector (not shown) may be used to detect a predetermined light intensity, so that the etching step is finished based thereon.

Then, using the same process container or another process container, plasma etching of the SiO<sub>2</sub> layer 201  
20 is performed through the opening pattern 203a of the photoresist layer, as in the operation of etching the organic antireflective layer 202. The etching gas used at this time is a gas of, e.g., C<sub>4</sub>F<sub>6</sub>, O<sub>2</sub>, and Ar, but it is not limited thereto.

25 As described above, when the plasma etching of the organic antireflective film 202 is performed through the opening pattern of the photoresist layer 203, SiF<sub>4</sub>

gas, which is a gas containing Si, is used. In this etching, a thin cured layer containing Si is formed on the surface of the photoresist layer 203, thereby improving the plasma resistance of the photoresist layer 203. As a consequence, during the etching of the organic antireflective layer 202, it does not suffer surface roughness increase or vertical stripe formation. In other words, the photoresist layer 203 of an ArF photoresist or F2 photoresist, which originally has a low plasma resistance, can maintain a high plasma resistance. In this case, where the etching gas for the organic antireflective layer 202 contains  $H_2$ , C=O bonds in the surface of the photoresist layer 203 are converted into C-C bonds or C=C bonds, which are chemically stronger. As a result, in cooperation with the thin cured layer containing Si, which is formed on the surface of the photoresist layer 203, the plasma resistance can be further improved.

Furthermore, as described above, after the etching of the organic antireflective layer 202, the etching of the  $SiO_2$  layer 201 disposed as an etching objective layer is performed through the opening pattern 203a of the photoresist layer 203. Since the plasma resistance of the photoresist layer 203 is improved during the etching of the organic antireflective layer 202, the plasma resistance remains high also in the plasma etching of the  $SiO_2$  layer 201 disposed as an etching

objective. As a consequence, the plasma etching can be performed, without incurring surface roughness increase or vertical stripe formation in the photoresist layer.

5       The etching objective layer is not limited to Si oxide, the representative of which is  $\text{SiO}_2$ , described above as an example. This embodiment may be applied to another Si compound, such as Si nitride or Si carbide, single-crystalline Si, poly-crystalline Si, organic material, organic-inorganic hybrid material, metal, or  
10       metal compound. Also, the structure of the plasma processing apparatus is not limited to that shown in FIG. 1.

Next, an explanation will be given of present examples according to this embodiment.

15       A process subject having the structure shown in FIG. 15 was used. Etching of the organic antireflective layer was performed, using various etching gas containing a substance having Si (present examples 9-1 to 9-7). Also, etching of the organic  
20       antireflective layer was performed, using various etching gas containing no substance having Si (comparative examples 9-1 and 9-2).

In the present examples and comparative examples, the first high-frequency power supply and second high-  
25       frequency power supply had frequencies of 60 MHz and 13.56 MHz, respectively. After the etching of the organic antireflective layer performed under the

following conditions according to the present examples and comparative examples, plasma etching of the SiO<sub>2</sub> layer was performed under etching conditions described later.

5            Etching of organic antireflective layer

(Present example 9-1)

Pressure in process container: 0.67 Pa (5 mTorr)

High-frequency power from first high-frequency  
power supply: 300W

10           High-frequency power from second high-frequency  
power supply: 60W

Etching gas and flow rate:

SiF<sub>4</sub> at 0.08 L/min (80 sccm)

(Present example 9-2)

15           Pressure in process container: 6.7 Pa (50 mTorr)

High-frequency power from first high-frequency  
power supply: 700W

High-frequency power from second high-frequency  
power supply: 100W

20           Etching gas and flow rate:

SiF<sub>4</sub> at 0.1 L/min (100 sccm)

(Present example 9-3)

Pressure in process container: 0.67 Pa (5 mTorr)

25           High-frequency power from first high-frequency  
power supply: 300W

High-frequency power from second high-frequency  
power supply: 60W



Etching gas and flow rate:

$\text{SiF}_4$  at 0.04 L/min (40 sccm)

$\text{CHF}_3$  at 0.04 L/min (40 sccm)

(Present example 9-4)

5 Pressure in process container: 0.67 Pa (5 mTorr)

High-frequency power from first high-frequency  
power supply: 300W

High-frequency power from second high-frequency  
power supply: 60W

10 Etching gas and flow rate:

$\text{SiF}_4$  at 0.04 L/min (40 sccm)

HBr at 0.04 L/min (40 sccm)

(Present example 9-5)

Pressure in process container: 0.67 Pa (5 mTorr)

15 High-frequency power from first high-frequency  
power supply: 300W

High-frequency power from second high-frequency  
power supply: 60W

Etching gas and flow rate:

20  $\text{SiF}_4$  at 0.04 L/min (40 sccm)

He at 0.04 L/min (40 sccm)

(Present example 9-6)

Pressure in process container: 0.67 Pa (5 mTorr)

25 High-frequency power from first high-frequency  
power supply: 300W

High-frequency power from second high-frequency  
power supply: 60W

Etching gas and flow rate:

$\text{SiF}_4$  at 0.04 L/min (40 sccm)

HBr at 0.02 L/min (20 sccm)

He at 0.02 L/min (20 sccm)

5 (Present example 9-7)

Pressure in process container: 6.7 Pa (50 mTorr)

High-frequency power from first high-frequency  
power supply: 1,000W

High-frequency power from second high-frequency  
10 power supply: 100W

Etching gas and flow rate:

$\text{SiF}_4$  at 0.03 L/min (30 sccm)

$\text{H}_2$  at 0.02 L/min (20 sccm)

(Comparative example 9-1)

15 Pressure in process container: 0.93 Pa (7mTorr)

High-frequency power from first high-frequency  
power supply: 100W

High-frequency power from second high-frequency  
power supply: 250W

20 Etching gas and flow rate:

$\text{CF}_4$  at 0.072 L/min (72sccm)

$\text{CHF}_3$  at 0.026 L/min (26 sccm)

$\text{O}_2$  at 0.006 L/min (6 sccm)

(Comparative example 9-2)

25 Pressure in process container: 6.7 Pa (50 mTorr)

High-frequency power from first high-frequency  
power supply: 1,000W

High-frequency power from second high-frequency  
power supply: 100W

Etching gas and flow rate:

$\text{CF}_4$  at 0.1 L/min (100 sccm)

5      Etching of  $\text{SiO}_2$  layer

(Present examples 9-1, 9-3 to 9-6, and comparative  
example 9-1)

Pressure in process container: 16 Pa (120 mTorr)

High-frequency power from first high-frequency  
10 power supply: 550W

High-frequency power from second high-frequency  
power supply: 350W

Etching gas and flow rate:

$\text{CF}_4$  at 0.1 L/min (100 sccm)

15       $\text{CHF}_3$  at 0.06 L/min (60 sccm)

(Present examples 9-2 and 9-7, and comparative  
example 9-2)

Pressure in process container: 2.7 Pa (20 mTorr)

High-frequency power from first high-frequency  
20 power supply: 1,800W

High-frequency power from second high-frequency  
power supply: 1,150W

Etching gas and flow rate:

$\text{C}_4\text{F}_6$  at 0.025 L/min (25 sccm)

25       $\text{O}_2$  at 0.026 L/min (26 sccm)

Ar at 0.7 L/min (700 sccm)

After performing the etching of the  $\text{SiO}_2$  layer 201,

as described above, the sectional shape of the etched portion of the process subject W was observed by means of electron micrograph in each of the present examples and comparative examples. As a result, in any of the present examples 9-1 to 9-7, the ArF photoresist layer 203 hardly showed surface roughness increase or vertical stripe formation. On the other hand, in any of the comparative examples 9-1 and 9-2, the ArF photoresist layer 203 showed surface roughness increase and vertical stripe formation.

(Tenth embodiment)

In this embodiment, the plasma processing apparatus 1 shown in FIG. 1 is used to subject a process subject W shown in FIG. 16A to a series of steps described below. This process subject W has an etching objective layer 211 consisting of Si oxide, a representative of which is an SiO<sub>2</sub> film, and a mask layer 212 of an ArF photoresist or F2 photoresist covering the etching objective layer 211. Also in this embodiment, the ArF photoresist or F2 photoresist may be made of an alicyclic group-containing acrylate resin, cycloolefin resin, cycloolefin-maleic anhydride resin, methacrylate resin or the like. In this embodiment, the showerhead or upper electrode plate 24 of the apparatus shown in FIG. 1 is made of Si.

The gate valve 32 is first opened, and the process subject W is transferred into the process container 2

and placed on the electrostatic chuck 11. Then, the gate valve 32 is closed, and the pressure in the process container 2 is reduced by the exhaust device 35. Then, the valve 28 is opened, and an inert gas, such as Ar, is supplied from the process gas supply source 30, thereby setting the pressure in the process container 2 at, e.g., 1.33 Pa (10 mTorr). As the inert gas, another gas, such as Kr or Xe, may be used. In this state, high-frequency powers are applied from the first and second high-frequency power supplies 40 and 50 to the upper electrode 21 and the lower electrode or susceptor 5 to ionize at least part of the inert gas, thereby sputtering the Si upper electrode plate 24. Before or after the timing when the high-frequency powers are applied to the upper and lower electrodes, a DC voltage is applied from DC power supply 13 to the electrode 12 in the electrostatic chuck 11 to electrostatically attract and hold the process subject W on the electrostatic chuck 11.

At this time, the high-frequency power applied to the upper electrode 21 provides energy for urging ionization of the inert gas. By sputtering the Si upper electrode plate 24, as described above, an Si-containing layer 213 is formed on the surface of the mask layer 212, as shown in FIG. 16B. If the time used to form Si-containing layer 213 on the surface of the mask layer 212 is too short, the plasma resistance

improvement effect can be hardly obtained. If the time is too long, a lot of Si-containing layer is formed on the surface of the etching objective layer 211 in the opening portion of the mask layer 212, and hinders the etching performed thereafter. Accordingly, it is preferable to select an appropriate value of the time. For example, this step may adopt conditions in which the upper electrode 21 is supplied with a high-frequency power having a frequency of 60 MHz at a power of 2,000W, while the susceptor 5 is supplied with a high-frequency power having a frequency of 2 MHz at a power of 100W. Under the conditions, it was confirmed that a range of 60 to 90 seconds was preferable for the processing time described above.

As regards the powers, the conditions described above reduced variation in the opening shape of the mask layer when the Si-containing layer was formed, as compared to a case where the power applied to the upper electrode was set at 1,250W, and the power applied to the susceptor was set at 400W (a so-called low  $V_{pp}$ ). If the  $V_{pp}$  is too high, the opening of the mask layer is expanded, thereby making it difficult to form holes or grooves in accordance with the designed opening pattern in the following etching step.

After the formation of the Si-containing layer on the surface of the mask layer is finished, the high-frequency powers stop being supplied.

Then, an etching gas is supplied into the process container 2, and high-frequency powers are applied to the upper electrode 21 and susceptor 5, to etch the etching objective layer 211. For example, where the etching objective layer 211 consists of Si oxide, a gas containing at least one selected from  $C_4F_6$ ,  $C_4F_8$ , and  $C_5F_8$  is preferably used. An example of such an etching gas is a mixture gas of  $C_4F_6$ ,  $O_2$ , and Ar. The pressure in the process container 2 is set at, e.g., 2.67 Pa (20 mTorr), and the high-frequency powers applied to the upper electrode 21 and susceptor 5 are set at, e.g., 1,600W and 800W, respectively. The frequencies of the high-frequency powers at this time are set at, e.g., 60 MHz and 2 MHz, respectively, as in the sputtering. The high-frequency powers are applied to turn the etching gas into plasma, thereby etching the etching objective layer 211 consisting of e.g., Si oxide. After the etching is finished, the etching gas and high-frequency powers stop being supplied.

The etching of the etching objective layer 211 of Si oxide was performed under the conditions described above. As a result, the selectivity of the etching objective layer 211 relative to the mask layer 212 (the etching rate of the etching objective layer / the etching rate of the mask layer) was 28.8. Where the etching was performed without the Si-containing layer formed on the surface of the mask layer 212, the

selectivity was 8.2.

The etching performed as described above is followed by a step (ashing step) of removing the mask layer 212 with the Si-containing layer formed on the surface thereof. In this example, a plurality of stages are used to remove the mask layer 212 with the Si-containing layer 213 formed on the surface thereof.

In the first stage, a gas containing fluorine, such as  $\text{CF}_4$ , is supplied into the process container 2, and high-frequency powers are applied to the upper electrode 21 and susceptor 5 for a predetermined time, to remove almost all the Si-containing layer 213 formed on the mask layer 212. This is done, because, if the Si-containing layer is left, Si-containing products may stick to the surface of the process subject after the mask layer 212 is removed in the next second stage. At this time, the pressure in the process container 2 is set at, e.g., 6.66 Pa (50 mTorr), and the high-frequency powers applied to the upper electrode 21 and susceptor 5 are set at, e.g., 1,600W and 800W, respectively, and have frequencies of, e.g., 60 MHz and 2 MHz, respectively, as in the sputtering. This process is performed under the conditions for, e.g., 90 seconds, to remove almost all the Si-containing layer 213.

Where a gas containing  $\text{CF}_4$ , and  $\text{O}_2$  and Ar added thereto was used at this stage, the mask layer 212 of



an ArF photoresist was damaged. Accordingly, it is preferable to use a gas containing only  $\text{CF}_4$ , or a gas containing  $\text{CF}_4$  with a small amount of  $\text{O}_2$  and Ar added thereto.

5           As a fluorine compound-containing gas, a gas other than  $\text{CF}_4$  may be used. However,  $\text{CF}_4$  is preferably used to suppress damage to the mask layer 212 of an ArF photoresist below the Si-containing layer 213.

10           In the second stage, a predetermined process gas is supplied, and high-frequency powers applied to the upper electrode 21 and the lower electrode or susceptor 5, to remove the mask layer 212 itself, in a state where almost all the Si-containing layer 213 has been removed. At this time, as a process gas, it is  
15           preferable to use a gas containing no fluorine compound, such as  $\text{O}_2$  gas only, or to use a mixture gas containing  $\text{O}_2$ ,  $\text{N}_2$ , and Ar, or a mixture gas containing  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{H}_2$ .

          A process according to this second stage was actually performed. In this case, the pressure, high-  
20           frequency powers, high-frequency power supply frequencies were not changed from the first stage, but only the process gas was changed, to perform ashing.  $\text{O}_2$  was used as the process gas. The process subject was observed after the mask layer 212 was removed. As a  
25           result, the opening shape and sectional shape of holes and grooves accorded with the design. Furthermore, there was no Si-containing product sticking to the

process subject.

In this embodiment, as described above, an inert gas is ionized by energy of high-frequency powers applied to the parallel-plate electrodes, to sputter the Si upper electrode plate 24. At this time, an Si-containing layer sticking to the surface of the mask layer 212 is formed to improve the plasma resistance of the mask layer 212 to be far better than that of the mask layer it self. Particularly, where the mask layer 212 is made of an ArF photoresist or F2 photoresist, which has a low plasma resistance, the plasma resistance improvement effect is remarkable.

In the ashing performed after the etching of the etching objective layer, a plurality of stages are performed to remove the Si-containing layer 213 and the mask layer 212 itself separately from each other. Accordingly, the removal operations can be respectively performed in accordance with the natures of the Si-containing layer 213 and mask layer. As a matter of course, the Si-containing layer 213 and mask layer 212 may be removed together. It is determined which to use, based on comparison in the total advantages and disadvantages between the removal using a plurality of stages and the removal performed at once.

A target used in sputtering to form the Si-containing layer on the mask layer is not limited to the upper electrode plate described above as an example.

The target may be another member, such as a focus ring, disposed in the process container and made of Si at least at a part of the surface. An Si member may be additionally disposed as the target. Another Si wafer  
5 having undergone no device processes (bare wafer) may be placed in the process container to use it as the target. Single-crystalline Si is preferable as Si of the target used in the sputtering.

In the example described above, the sputtering is  
10 performed in a parallel-plate type apparatus for plasma etching, using high-frequency energy, but it is not limited thereto. Another structure may be adopted, as long as the structure can apply energy to ionize at least part of an inert gas. For example, microwave  
15 energy may be used in place of high-frequency energy as the energy for the same. Even where high-frequency energy is used, a system of applying a high-frequency power from an antenna to form an induction  
electromagnetic field may be used, in place of the  
20 parallel-plate type.

A method of forming the Si-containing layer 213 on the surface of the mask layer 212 is not limited to sputtering. For example, CVD may be used to form the Si-containing layer 213 on the surface of the mask  
25 layer 212. Where CVD is used to form the Si-containing layer 213, an organic silane group gas or inorganic silane group gas may be used as a raw material gas. Of

them, an inorganic silane group gas is preferable. In this case, CVD can be performed with the gas, in accordance with a common procedure.

5 A method of adding an Si compound, such as  $\text{SiF}_4$ , to the etching gas may be adopted as a method of forming the Si-containing layer 213 on the surface of the mask layer 212. With this arrangement, it is possible to improve the plasma resistance of the mask layer 212 of an ArF photoresist or F2 photoresist, and to etch the  
10 etching objective layer 211, at the same time.

In this embodiment, the etching objective layer is not limited to Si oxide described above. The etching objective layer may be selected from various materials, such as SiC, SiN, organic low dielectric constant  
15 material, SiOF, metal, and metal compound. It should be noted, however, since the layer formed on the surface of the mask layer contains Si as the main component, it is difficult to apply this embodiment to a process subject that includes an Si etching objective  
20 layer. This is so, because, where the mask layer surface and etching objective layer consist of the same material, their etching rates become almost the same. The mask layer is not limited to a photoresist material having a low plasma resistance, such as an ArF  
25 photoresist or F2 photoresist. Another organic photoresist layer, or another mask layer other than photoresist may be used.